

# PATENT SPECIFICATION

DRAWINGS ATTACHED



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## COMPLETE SPECIFICATION

### Improvements in the Manufacture of Isocyanates

We, ETAT FRANCAIS, represented by the Secretary of State for Defence and for the Armed Forces (Powder Department), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

It is well known that one of the methods for producing isocyanates consists in causing phosgene to act on a substance containing at least one amine group.

Said method has generally been executed as follows: the amine has been introduced either in its free state or in the form of salts readily decomposable into such amines while forming a solution or a suspension at room temperature into pure or dissolved phosgene. This leads to the formation of a compound substance generally insoluble in the medium carrying it. Gaseous phosgene is introduced into the mixture which is simultaneously heated so as to decompose said compound substance and after releasing the gases at a high temperature of about 100 to 180° C. the desired isocyanate is obtained as a solution in the solvent used, the yield being equal to about 70 to 85% in most cases.

It has also been proposed to carry out the method in an autoclave or digester, in order to increase the yield, and to reduce the reaction time.

According to the present invention, a process for the continuous preparation of aromatic isocyanates by the reaction of a solution of amine in the free state or in the form of salts easily decomposable into such amines, in an inert solvent, and a solution of phosgene in excess which is injected under a pressure greater than 3 kgs. per sq. cm., is characterised by the fact that the reactants are introduced simultaneously, while being mixed energetically, into the lower end of a tubular reactor in which the reaction products are caused to move rapidly to the upper end where, without re-cycling, the

whole of the liquid phase is collected in a container from which it passes for the isocyanate to be extracted.

In this container, which is kept under pressure, excess phosgene is evolved and hydrochloric acid formed; these gases pass to and through a condenser and the phosgene is liquefied by cooling with water.

The reaction mixture flowing from the container and including a little phosgene and hydrochloric acid, is caused to expand inside another container which is subjected to atmospheric or reduced pressure.

This last-mentioned container is heated to a temperature higher than that of the preceding reactor and the reaction mixture flows out preferably as a film through said heated container, the remaining excess phosgene and hydrochloric acid being released and then condensed by any suitable means.

The isocyanate formed is finally separated from its solvent by distillation of the liquid collected at the outlet of the said heated container.

In order that the invention may be better understood, it will now be described with reference to the accompanying diagrammatic drawings, which are given by way of example only and in which:—

Fig. 1 is a general diagrammatic view of an arrangement for the production of aromatic isocyanates according to the invention, and

Fig. 2 shows a detail modification thereof. In Fig. 1, 1 and 2 designate respectively the feed containers filled respectively with pure or dissolved phosgene and with a solution of amine in its free state or in the form of a salt readily decomposable into such amines in an inert solvent.

Said containers 1 and 2 are connected respectively through the pipes 3 and 4 and through the revolution meters or flow meters 5 and 6 with the injection pumps 7 and 8 which provide for the injection under pressure of the phosgene and of the solution of

amine in its free state or in the form of a salt readily decomposable into such amines, in the desired relative proportions inside a chamber 9 subjected to pressure, communicating in its turn with a reaction vessel constituted by the column 10.

Electromagnetic or supersonic stirring means may be fitted inside the chamber 9 and/or at the lower end of the column 10 for furthering the agitation of the mixture.

This mixing system may be replaced by a venturi input nozzle which effects an excellent commingling. Such a modification has been illustrated in Fig. 2 and on a larger scale. This modified arrangement includes two input-nozzles *a* and *b* of which one serves for feeding the hereinbefore defined amine solution delivered by the pump 8 of Fig. 1 while the other nozzle *b* feeds the phosgene solution delivered by the pump 7 or inversely, the two liquids being intimately commingled in the neck of the convergent-divergent nozzle and forcibly flowing out together at *c* into the reaction column 10, the mixing chamber 9 being omitted in this case.

In both cases, the reaction column 10 fed by the chamber 9 or by the output nozzle *c* of the venturi illustrated in Fig. 2 may be given a height of about 5 or 6 meters. This reaction column may consist of one or more tubes which are cooled or heated through external means according to requirements and which are capable of resisting pressure; it is possible to use for instance a rectilinear tube provided with a jacket 11 as illustrated or again a spiral tube could be used immersed in a bath which is brought to the desired temperature.

The upper end of this reaction column opens into a gas-releasing chamber 12 provided with an overflow pipe 14 at a level 13. In said overflow pipe is inserted a pressure-releasing valve 15 ahead of a heating column 16 for the purpose hereafter disclosed.

A pipe 17 starting from the upper end of said column 16 serves for exhausting the hydrogen chloride evolved therein while the lower end of the column 16 communicates with the outflow channel 18 for the removal of the aromatic isocyanate solution freed of its gases. The upper end of the gas releasing chamber 12 opens into a pipe 19 passing through a condenser 20 and leading into a collector chamber 21 which may be connected directly in its turn through a channel 22 with the mixing chamber 9 for recycling the phosgene evolved in the chamber 12; furthermore, a branch pipe 23 provided with a pressure-releasing valve 24 is connected with the pipe 19 between the condenser 20 and the collector chamber 21 and serves for exhausting the gases towards absorbing means, not illustrated, operating under atmospheric pressure. Lastly a safety valve 25

is provided in the gas releasing chamber 12.

The operation of the arrangement is as follows: the phosgene and the hereinbefore defined amine fed by the containers 1 and 2 are measured out by the pumps 7 and 8 respectively and enter, through the venturi of Fig. 2 or the mixing chamber 9 of Fig. 1 into the reaction column 10 in which they rise continuously and quickly while subjected to reaction temperature. This temperature ranges between 80 and 200° C. according to the amine used. As to the pressure applied, it is equal to 3 kg. per sq. cm. at a minimum and at the maximum, it is equal to the vapour pressure prevailing inside the chamber 12 at the temperature of the latter. In practice, it is preferably equal to 15 to 20 kg. per sq. cm. Such a pressure allows the reaction to be executed speedily within a few minutes. The reaction liquid containing the aromatic isocyanate flows then continuously through the pressure-reducing valve 15, and after expansion down to atmospheric pressure or if required to well below atmospheric pressure, it enters the column 16 incorporating a suitable filling or helically coiled member heated to a suitable high temperature so as to decompose the intermediate compound substances produced and to release the gases formed in the reaction product. The hydrogen chloride escapes through the pipe 17 and this continuous removal of the gases out of the liquid film flowing through the chamber 16 completes the reaction. The aromatic isocyanate passing out at 13 is fed directly to the usual distillation means, not illustrated.

The gases released inside the chamber 12, which contain the excess phosgene and some hydrogen chloride stream out through the pipe 19 into the condenser 20 where the phosgene is condensed at the pressure prevailing inside the system 9, 10, 12, 20, 21, to be collected in the vessel 21 from which it may be recycled if required in its liquid state into the mixing chamber 9 through the pipe 22. The gases carried along with the liquefied phosgene escape through the pressure-reducing valve 24 towards any suitable absorbing means operating under atmospheric pressure.

The use of pressure-reducing or gauged valves 15, 24, 25 allows maintenance of the desired pressure throughout the system including the mixing chamber 9, the gas-releasing chamber 12, the pipe 19 and the condenser 20.

The arrangement according to the invention permits of producing in a continuous manner aromatic isocyanate with a small bulk apparatus and little labour, while giving excellent yields which may rise beyond 95% with reference to the original amount of the defined amine. In practice, there is used for the defined amine an amount of phosgene

equal to or higher than the theoretical amount. The excess of phosgene is exhausted with the gases evolved either in the chamber 12 or in the column 16. It is an advantage of the system that the gases from the chamber 12 are condensed under pressure before expansion thereof. This condensation allows recovering in its liquid state a large fraction of the excess phosgene evolved out of the reaction mixture, so that it may be immediately recycled as mentioned, into the mixing chamber 9, or into the reaction column 10 under the action of hydrostatic pressure. As the circuit is held under pressure, the condensation may be ensured by cooling simply by water instead of brine.

We will now disclose by way of examples two selected practical applications of our invention.

#### EXAMPLE 1

We use flowmeters or revolution meters for introducing a hot solution of tolylene diamine (one part by weight) in four parts by weight of tricresyl phosphate and a solution of 2.4 parts by weight of phosgene in two other parts of tricresyl phosphate through two corresponding measuring pumps into the mixing chamber 9 and reaction column 10 as a continuous flow. The exothermic reaction takes place inside said chamber without any attempt at slowing it down so that the reaction mixture is brought to about 70° C., the pressure prevailing throughout the apparatus being equal to 20 kg. per sq. cm. This pressure is maintained at an unvarying value, as provided by the continuous exhaust of the gases and liquid. The latter runs them in film formation inside the heating column 16 provided with a helically coiled member heated through external means to a temperature ranging between 130 and 170° C.; the liquid film thus running downwardly inside the column 16 is subjected to a pressure reduced to 200 gr. per sq. cm. There is obtained at the lower end of the column a coloured product, from which by subsequent rectification is obtained with a yield of 90% tolylene diisocyanate, the boiling point of which is 125° C.

#### EXAMPLE 2

The procedure is the same as in the case of Example 1 except for the fact that there is used a solution of phosgene and a solution of aniline, the solvent being in both cases ethyl phthalate. The temperature of reaction with phosgene at raised temperature is equal to about 95° C. under a pressure of 20 kg. per sq. cm. with a temperature of 125° C. for the release of the gases under a pressure of 800 gr. per sq. cm.; the isocyanate obtained with a yield of 97% has a boiling point 90° C.

#### WHAT WE CLAIM IS:—

1. A process for the continuous preparation of aromatic isocyanates by the reaction

of a solution of amine in the free state or in the form of salts easily decomposable into such amines in an inert solvent, and a solution of phosgene in excess which is injected under a pressure greater than 3 kgs. per sq. cm., characterised by the fact that the reactants are introduced simultaneously, while being mixed energetically, into the lower end of a tubular reactor in which the reaction products are caused to move rapidly to the upper end where, without re-cycling, the whole of the liquid phase is collected in a container from which it passes for the isocyanate to be extracted.

2. A process as claimed in Claim 1 in which the container in which the liquid phase is collected is in the form of a gas releasing vessel operating substantially under the same pressure and communicating with the outlet through an overflow pipe provided with a pressure reducing valve.

3. A process as claimed in Claims 1 and 2, in which the unreacted phosgene evolved under pressure is cooled, preferably by water, so as to return to its liquid condition and to be re-cycled to the reaction stage, the hydrogen chloride admixed with the cooled phosgene being allowed to expand and separately exhausted.

4. A process as claimed in Claim 2, in which the overflow pipe provided with a pressure reducing valve passes to a heated column operating under atmospheric or sub-atmospheric pressure and at a raised temperature, from which the reaction mixture flows out after having released therefrom the remaining excess phosgene and hydrochloric acid which pass off in the gaseous phase for subsequent condensation.

5. A process as claimed in Claim 1, including means for feeding the reactants, comprising either a common or separate pumps feeding said reactants into the tubular reactor and subjected to the same pressure as the latter.

6. A modification of the process as claimed in Claim 5, wherein the reaction components are fed directly by a Venturi into the tubular reactor, said Venturi preferably being provided with separate inlets for the two reaction components.

7. A process as claimed in any of the Claims 2 to 6, including a re-cycling channel for the excess phosgene passing out of the gas releasing vessel, said channel including a water-cooled condenser and terminating in a phosgene collecting chamber, in turn communicating with the tubular reactor, a branched channel with a relief valve being connected to the re-cycling channel between the condenser and the phosgene collecting chamber, for the exhaust of the hydrogen chloride carried along by the phosgene.

8. A process as claimed in any one of the preceding claims, including electromagnetic

or supersonic means at the lower end of the tubular reactor for the agitation of the reaction mixture.

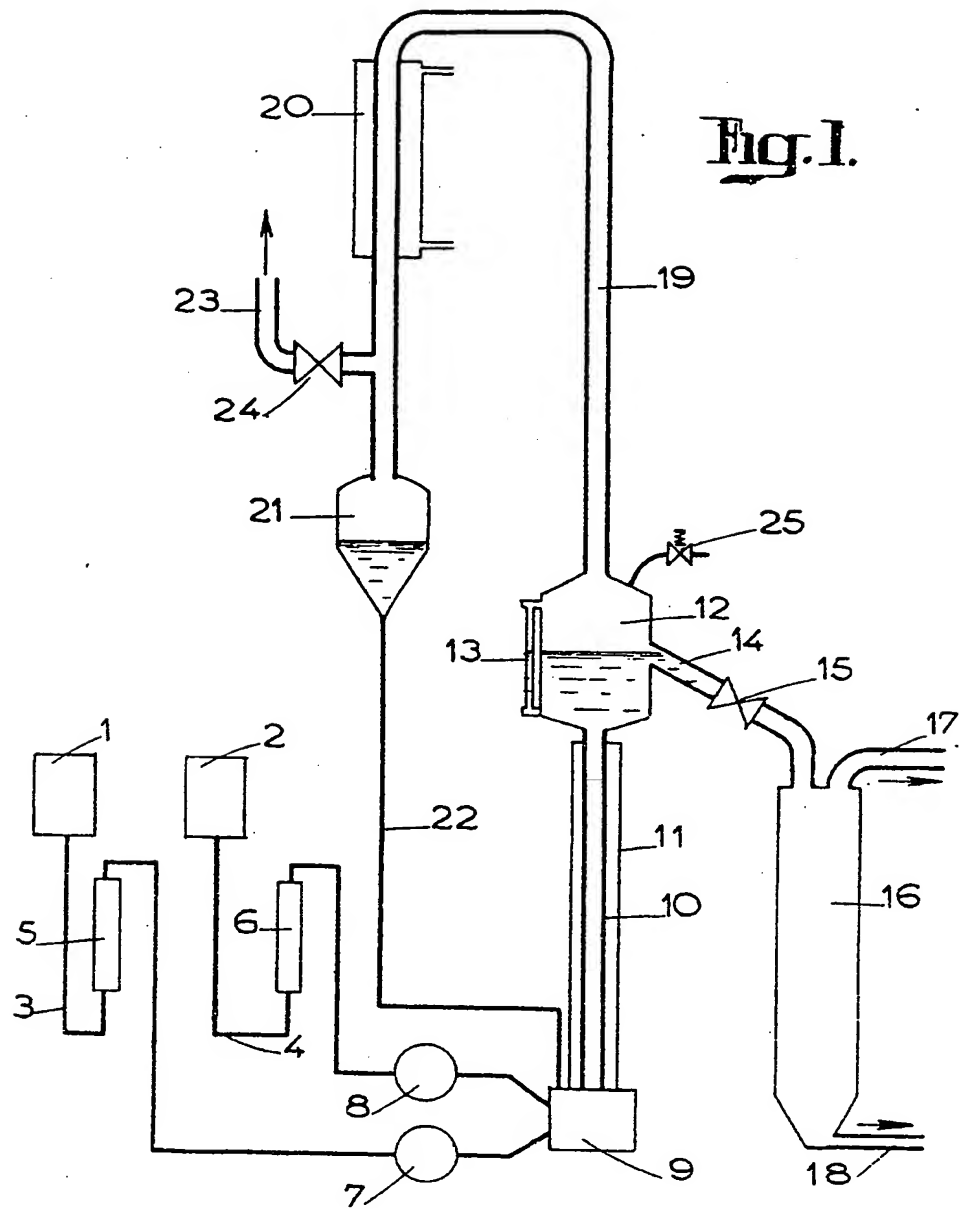
- 5 9. A process and means for producing isocyanates by reaction under pressure between phosgene and an amine in the free state or in the form of a salt easily decomposable into

such amine, substantially as described with reference to and as illustrated in the accompanying drawings.

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**Fig. 1.**

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2 SHEETS

COMPLETE SPECIFICATION  
This drawing is a reproduction of  
the Original on a reduced scale.  
SHEETS 1 & 2

I.

